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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Infrared Anisotropy and Structure of Crystalline Form C Stearic Acid and Vaccenic Acid[2]

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The infrared spectra of highly oriented crystalline films of form C stearic acid and of vaccenic acid have been obtained using polarized radiation with the plane of polarization perpendicular and at 45° angles to the principal crystal planes. The anisotropy of stearic acid is discussed in relation to its known structure. The data obtained on vaccenic acid indicate that the substance crystallizes in the orthorhombic system. The factor group of the space group is probably isomorphous with D_{2h}. The main portions of the hydrocarbon chains are packed into an orthorhombic substructure similar to polyethylene and form C saturated acids, but the chains seem twisted near the double bonds, which appear to be nearly parallel in the projection along the *C*-axis.

Introduction

The structure of saturated long chain monocarboxylic acids in their various crystallographic forms is known from single crystal X-ray measurements.[3] Very few data are available on the structure of the corresponding mono- and polyunsaturated compounds. Lutton and Kolp[4] have concluded from long spacing measurements obtained from powder diffraction data that in the *trans*-6- through *trans*-12-octadecenoic acids the hydrocarbon chains of the odd compounds are roughly perpendicular to the planes containing the carboxyl groups, whereas the chains of the even compounds are tilted. Odd and even refer to the number of carbons from the carboxyl group to the double bond.

(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented in part at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1958.

(3) E. v. Sydow, *Arkiv. Kemi*, **9**, 231 (1956).

(4) E. S. Lutton and D. G. Kolp, THIS JOURNAL, **73**, 2733 (1951).

No polymorphism was observed by these authors. The members of the odd series appear particularly interesting and worthy of further study, since the straight chains suggest a packing substantially different from the known (tilted) structures of the corresponding saturated compounds.

The present study was undertaken (a) to relate the infrared anisotropy of form C stearic acid, a typical saturated long chain monocarboxylic acid, to its known structure and to earlier band assignments, and (b) to deduce structural information for the corresponding *trans*-11,12-monounsaturated compound, vaccenic acid, from infrared anisotropy measurements. Although theoretical methods for treating the infrared spectra of molecular crystals are well established,[5,6] it has been reported that polarization measurements on high molecular weight compounds sometimes lead to anomalous results.[7] The data obtained in this work should contribute to a general evaluation of such measurements. The infrared absorption bands associated with the COOH and COOD groups in dimeric carboxylic acids in general[8,9] and with long chain monocarboxylic acids in particular[10-12] have been discussed by earlier investigators. Studies with polarized infrared radiation have been reported on adipic acid[13,14] and on eicosanoic acid.[15] Evaluation of the results has been confined to a discussion of the CH and OH stretching bands of adipic acid,[14] based on an oriented gas model, and to a discussion of the 1180–1300 cm.$^{-1}$ region of eicosanoic acid.[16] The packing and shape of carboxylic acid molecules in the crystalline state has not been extensively studied by infrared methods, although it has been observed that various polymorphic forms show marked differences in absorption[10,17] and that conclusions about the packing of the hydrocarbon chains can be drawn from the shape of the CH_2 rocking band around 720 cm.$^{-1}$.[18]

Experimental

Crystals of saturated straight chain fatty acids usually grow in thin plates, the molecules being arranged in sheets which are held together by hydrogen bonds in the carboxyl group layers and weak van der Waals forces in the methyl layers. The hydrocarbon chains, attached through strong van der Waals forces to one another, form angles ranging from 56 to 66° with these layers (and with the well developed (001) faces).[3] Very thin, highly oriented specimens suitable for infrared investigation were prepared by melting a small amount of sample between 1.5 × 5 cm. rock salt plates and cooling the resulting sandwich under a temperature gradient produced by placing one end of it on a warm electric plate and the other on a metal block cooled with ice-water. Crystallization started at the cool end and proceeded slowly toward the warmer end. The method is similar to the one used by Halverson and Francel on malononitrile.[19] Under these conditions the carboxyl group layers (and the (001) faces) align themselves parallel to the rock salt plates. The *b*- or the *a*-axis is found to be along the direction of crystal growth. The specimens were placed in the radiation beam of a Perkin–Elmer Model 21 instrument equipped with sodium chloride optics and a silver chloride polarizer in such a way as to relate the electric vector of the radiation beam to the crystallographic axes in the various ways shown in Fig. 1. Small 45° NaCl prisms were placed on either side of the sample for measurements with the radiation beam at 45° angles to the plane of the sample. The *a* and *b*, a′ and a″, b′ and b″ pairs of spectra were obtained on one and the same sample, but slight differences in thickness are possible between the samples used for obtaining the various pairs. Information about the polarization characteristics of the individual absorption bands and the structure of the solid aggregate was deduced from internal comparison of the six obtained "views." In the case of monoclinic form C stearic acid, the *a*- and *b*-axes were identified by comparison of the two pairs of spectra obtained with tilted samples. The spectra obtained with the electric vector along the *a*- and *b*-axes were subsequently used to classify a band as A_u or B_u, whereas a comparison of spectra obtained with the electric vector along *a*, a′ and a″ was used to estimate the direction of the B_u vectors within the plane perpendicular to the monoclinic *b*-axis. In the case of orthorhombic vaccenic acid (see below) the spectra obtained with the electric vector along *a*, a′, *b*, b′ were utilized to determine the polarization characteristics of any observed absorption band with respect to the mutually perpendicular crystallographic axes. The *a*- and *b*-axes of vaccenic acid were named in analogy with stearic acid, the designation being based on the polarization of the bands arising from the hydrocarbon substructure (*e.g.*, the 720 cm.$^{-1}$. CH_2 rocking band was said to be polarized along the *b*-axis). The wide slits which had to be used because of the energy loss caused by the polarizer and the close spacing and frequent overlap of absorption bands made quantitative intensity measurements very difficult. In some instances it was nevertheless possible to draw qualitative conclusions about the shape and packing of individual molecules from intensity comparisons between differently polarized branches of bands arising from the same molecular vibration. When polarized radiation is used, complications arising from birefringence are possible,[7] but none are expected for measurements on (orthorhombic) vaccenic acid with the electric vector parallel to *a* or *b*. These were the data used for drawing conclusions about the shape of individual molecules. Other measurements, where the above conditions were not met (including measurements obtained with "tilted" light beams) yielded data which were internally consistent. In the case of stearic acid these data were in agreement with the known structure of the substance, bands which could be assigned with reasonable certainty showing predictable polarization.

A purified and recrystallized commercial sample of stearic acid (Atlas Powder Company) was used. The sample of vaccenic acid was obtained through the courtesy of Professor J. B. Brown of the Ohio State University.

Results and Discussion

Stearic Acid.—Figure 2A shows the spectra of form C stearic acid obtained with the electric vector parallel to the *a*- and the *b*-axes, 2B with the electric vector along a′ and a″ (compare with Fig. 1). The spectra obtained with the electric vector along b′ and b″ were identical, as predicted by the monoclinic symmetry of the sample. They do not otherwise contribute to interpretation and are therefore not shown. Table I lists the observed bands, their approximate intensity, polarization and assignment.

(5) D. F. Hornig, *J. Chem. Phys.*, **16**, 1063 (1948).
(6) H. Winston and R. S. Halford, *ibid.*, **17**, 607 (1949).
(7) M. C. Tobin, *J. Phys. Chem.*, **61**, 1392 (1957).
(8) D. Hadži and N. Sheppard, *Proc. Roy. Soc.* (*London*), **A216**, 247 (1953).
(9) S. Bratož, D. Hadži and N. Sheppard, *Spectrochim. Acta*, **8**, 249 (1956).
(10) R. G. Sinclair, A. F. McKay and R. N. Jones, This Journal, **74**, 2570 (1952).
(11) R. N. Jones, A. F. McKay and R. G. Sinclair, *ibid.*, **74**, 2575 (1952).
(12) R. G. Sinclair, A. F. McKay, G. S. Myers and R. N. Jones, *ibid.*, **74**, 2578 (1952).
(13) J. Mann and H. W. Thompson, *Proc. Roy. Soc.* (*London*), **A192**, 489 (1948).
(14) E. J. Ambrose, A. Elliot and R. B. Temple, *ibid.*, **A206**, 192 (1951).
(15) A. R. H. Cole and R. N. Jones, *J. Opt. Soc. Amer.*, **42**, 348 (1952).
(16) Eldon E. Ferguson, *J. Chem. Phys.*, **24**, 1115 (1956).
(17) E. v. Sydow, *Acta Chem. Scand.*, **9**, 1119 (1955).
(18) D. Chapman, *J. Chem. Soc.*, 4489 (1957).
(19) F. Halverson and R. J. Francel, *J. Chem. Phys.*, **17**, 964 (1949).

TABLE I

SPECTRUM AND POLARIZATION OF FORM C STEARIC ACID, 4000-650 CM.$^{-1}$

Cm.$^{-1}$	I[a]	Polarization[b]		Description
2954	vw	ac	B_u	CH$_3$ asym. str.
2948	vw	b	A_u	
2921	s	ac $\perp$	B_u	CH$_2$ asym. str.
2916	s	b	A_u	
2900[c]	s	ac $\parallel$[d]	B_u	OH str. + unres. comb.
2849	m	b	A_u	CH$_2$ sym. str.
2846	m	ac $\perp$	B_u	
2660	sh	ac	B_u	comb. involving I.R. inactive modes
2640	sh	b	A_u	
1707	vs	b	A_u	C=O str.
1702	vs	ac[d]	B_u	
1692	vs	b	A_u	
1474	m	ac $\perp$	B_u	CH$_2$ bend.
1466	m	b	A_u	
1442	w	b	A_u	C–O str. (OH bend.)
1433	s	ac $\parallel$[d]	B_u	
1412	m	b	A_u	α-CH$_2$ bend.
1408	m	ac	B_u	
1376	w	ac		CH$_3$ bend.
1357	w			
1348	w			
1331	w			
1313	w			
1299	m	b, ac		
1280	m	$\perp$ to a[e]		
1261	m			
1241	m			
1221	m			
1203	m			
1187	m			
1300	s	b, ac[d]	B_u, A_u	OH bend. (C–O str.)
1120	vw			
1103	w	b, ac		C–C ?
1070	vw			
941	s	ac $\perp$[d]	B_u	out-of-plane OH bend.
939	s	b	A_u	
907	w	ac $\parallel$		
810	w	b, ac $\perp$		CH$_2$ rock.
783	vw	b, ac $\perp$		
760	w	b, ac $\perp$		
728	s	ac $\perp$	B_u	
720	s	b	A_u	
685	w	ac $\parallel$[d]	B_u	COO def.

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder. [b] ac, in the *ac*-plane; b, along monoclinic axis; $\perp$, essentially perpendicular to hydrocarbon chains; $\parallel$, essentially parallel to hydrocarbon chains. [c] Approximate center of very broad band overlapping with CH bands. [d] Polarization of B_u carboxyl modes discussed in text. [e] Higher frequency bands "tilted" toward $\parallel$, lower frequency bands toward $\perp$.

Evaluations of single crystal X-ray data of long chain aliphatic compounds frequently make use of the concept of a subcell which describes the repetition in and of the hydrocarbon chains.[3,20,21] It appears logical to apply a similar approach to the interpretation of infrared absorption data. Form C saturated fatty acids belong to the space group C^5_{2h} with four molecules in the unit cell.[3] The packing of the hydrocarbon chains can be described in terms of an orthorhombic subcell which has been analyzed

(20) A. Müller, *Proc. Roy. Soc.* (*London*), **A114**, 542 (1927).

(21) V. Vand, *Acta Cryst.*, **4**, 104 (1951).

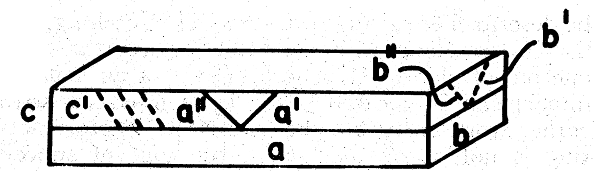

Fig. 1.—Orientation of the electric vector with respect to the sample: c', direction of the main axes of the hydrocarbon chains of form C stearic acid; c, direction of the main axes of the hydrocarbon chains of vaccenic acid; *a*, *b*, a', a'', b', b'', directions of the electric vector of the radiation beam.

by Bunn[22] and contains four CH$_2$ units. The hydrocarbon chains are tilted 56° with respect to the layers of the carboxyl groups.[3]

Four doublets arising from eight infrared-active factor modes of the orthorhombic subcells are easily located by comparison with polyethylene.[23] They can be described as B_{1u} and B_{2u} CH$_2$ in-phase stretching, out-of-phase stretching, bending and rocking vibrations. If the orthorhombic subcells are regarded as built into the monoclinic main structure, the B_{2u} modes are polarized along the monoclinic *b*-axis. The B_{1u} and B_{3u} modes are polarized in the plane perpendicular to the monoclinic *b*-axis in directions perpendicular to the chains and along the chains, respectively. The observed polarization of the eight observed subcell bands is in agreement with prediction.

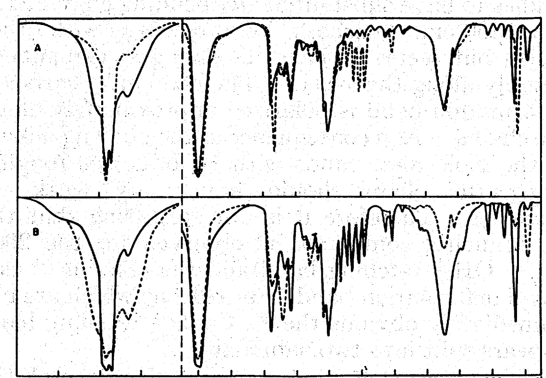

Fig. 2.—Infrared spectrum of form C stearic acid: A, electric vector along *a* (solid line) and *b* (dotted line); B, electric vector along a' (solid line) and a'' (dotted line); *cf.* Fig. 1.

The four carboxyl groups in the main cell can be regarded as two six-membered rings with C_{2h} symmetry, located on two C_i sites of the C^5_{2h} space group.[24] The nine infrared active fundamentals of a (hypothetical) isolated carboxyl dimer,[8] of which six should appear in the investigated region,[8,9] split under these conditions each into an A_u and a B_u mode. The A_u modes should be polarized along the monoclinic *b*-axis, the B_u modes in the plane perpendicular to this axis, but otherwise in a direction determined by the structure of the groups, their arrangement in the crystal and the particular mode involved. The position of these bands (which can

(22) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

(23) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).

(24) R. S. Halford, *ibid.*, **14**, 8 (1946).

be described as arising from one OH stretching, one C=O stretching, three COOH deformation and one out-of-plane OH bending mode of an isolated dimer) can be located easily by comparison with earlier work on carboxylic acids.[8–12] Factor splitting is not as obvious as in the case of subcell modes, but could be observed on the C=O stretching band around 1700 cm.$^{-1}$, the 1430 cm.$^{-1}$ region band and the OH bending band around 940 cm.$^{-1}$. A description of the approximate polarization of the B_u modes in the *ac*-plane is given. The broad band associated primarily[9] with OH stretching is polarized roughly along the chains. The B_u component of the out-of-plane OH bending mode is perpendicular to the OH stretch, as expected. The very strong C=O stretching band, having strong, but not identical, components along both the a′ and the a″ directions, must be polarized in a direction close to, but not quite along the *a*-axis. These observations are in agreement with the structure of form C acids and with the description of the three modes as localized bond vibrations. The polarization of the three mixed[8] deformation modes does not have to be even approximately related to any bond direction. It is nevertheless interesting to note that the 1433 cm.$^{-1}$ band is polarized roughly parallel to the OH stretching band. This speaks against its characterization as an OH bending mode, although in formic acid the highest deformation mode has been found by deuteration studies to have substantial OH bending character.[25] The 1300 cm.$^{-1}$ carboxyl band overlaps with other bands but seems to have its strongest component roughly along the *a*-axis. The 685 cm.$^{-1}$ carboxyl deformation band is polarized approximately along the chains. As a consequence of the known packing of the molecules, bands with B_u branches roughly along the chain should have very weak A_u branches. Therefore it is not surprising that the A_u branches could not be observed for the 2900 cm.$^{-1}$ OH stretching band and the 685 cm.$^{-1}$ carboxyl deformation band. For reasons which are not immediately obvious the A_u C=O stretching band appears split into two submaxima.

This covers the nine strongest bands and the weak band at 685 cm.$^{-1}$. Of the remaining bands the three weak maxima between 760 and 810 cm.$^{-1}$ can be assigned to unresolved CH_2 rocking doublets[26] (inactive in indefinitely long chains), the doublet around 1410 cm.$^{-1}$ to a bending vibration of the α CH_2 unit,[27] two very weak bands in the 2900 cm.$^{-1}$ region to stretching modes and the weak 1376 cm.$^{-1}$ band to a bending mode of the CH_3 end groups. The polarization of these bands (as far as it could be determined) is in agreement with the assignments. The weak 2660 and 2640 cm.$^{-1}$ shoulders on the main OH stretching band probably arise from combinations of the *ungerade* (infrared active) and *gerade* (Raman active) carboxyl modes around 1300 and 1430 cm.$^{-1}$.[9] Two groups of weak to medium bands in the 1070–1120 and 1187–1357 cm.$^{-1}$ regions remain. The A_u, B_u pairs could not be resolved with available instrumentation. No definite conclusions seem possible at present about the origin of these groups of bands. A few pertinent observations are listed below.

The highest frequency (1357 cm.$^{-1}$) band of the upper series has a B_u component approximately parallel to the chains and is close to a (weak) polyethylene band assigned by various investigators[23,28,29] to the CH_2 wagging mode. The remaining, almost equally spaced bands of this series, which have been assigned to coupled CH_2 wagging and/or twisting modes in fatty acids,[10–12] are

TABLE II

SPECTRUM AND POLARIZATION OF VACCENIC ACID, 4000-650 CM.$^{-1}$

Cm.$^{-1}$	I[a]	Polarization[b]	Description
3140	s	**c**, a[c]	OH str. + unres. comb.
3015	sh	b	=C—H str.
2953	vw	a[d]	CH_3 asym. str.
2949	vw	b	
2920	s	a	CH_2 asym. str.
2914	s	b	
2848	m	b	CH_2 sym. str.
2846	m	a	
2650	sh	a, b	Comb. involving I.R. inactive modes
1714	s	b	C=O str.
1701	s	a	
1470	s	a	CH_2 bend.
1461	s	b	
1457	vw	a ?	
1448	m	c	C–O str. (OH bend.)
1439	w	b	
1420	m	b	α-CH_2 bend.
1411	m	a	
1377	w	c, a, b	CH_3 def.
1352	w	c	CH_2 wag. ?
1341	w	c	
1322	w	c(b)	
1313	w	c	
1301	m	**c** > b > a	
1275	m		
1248	m		
1218	m		
1190	m		
1118	vw	**a**, b, c	C–C ?
1102	w	**a**, b, c	
1092	w	a	
1069	w	**c**, a	
970	w	b	=C—H out-of-plane bend.
965	s	**a** ≫ c	
940	w	b	
936	w	a	
885	m	b	OH out-of-plane bend.
877	m	a	
802	w	a, b	CH_2 rock. ?
729	m	a	CH_2 rock.
720	m	b	
686	w	**c** ≫ a	COO def.

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder. [b] a, b, c—along the *a*-, *b*-, *c*-axis. [c] If (unresolved) branches are present along more than one axis, the strongest component is boldfaced. [d] If unresolved or strongly overlapping branches along both *a* and *b* are present, presence or absence of a *c* branch could not be determined with certainty.

(25) R. C. Millikan and K. S. Pitzer, *J. Chem. Phys.*, **27**, 1305 (1957).

(26) R. G. Snyder, *ibid.*, **27**, 969 (1957).

(27) S. A. Francis, *ibid.*, **19**, 942 (1951).

(28) J. Rud Nielsen and A. H. Woollett, *ibid.*, **26**, 1391 (1957).

(29) O. Theimer, *ibid*, **27**, 1041 (1957).

polarized neither perpendicular, nor parallel to the chains, in contrast to the previously discussed CH_2 modes which show predictable polarization. The B_u components appear to be roughly perpendicular to the *a*-axis, with higher frequency bands "tilted" toward a parallel direction, lower frequency bands toward a perpendicular direction. Ferguson's[16] conclusion that this series of bands is polarized the same way as the CH_2 rocking band around 720 cm.$^{-1}$ holds for the A_u components. The eicosanoic acid spectra on which his conclusion was based[15] were obviously obtained with the electric vector parallel to the *a*- and the *b*-axes. The B_u components, which are roughly perpendicular to both the *a*- and *b*-axes, but not to the main axes of the hydrocarbon chains, were under these conditions not observed. The polarization of the 1187–1357 cm.$^{-1}$ bands constitutes the main notable deviation from the general pattern which is in agreement with the model of (independent) layers of end groups built into a regular hydrocarbon structure. This agrees with previous observations[11] that the number, intensity and spacing of these bands likewise depends on the nature of end groups and the hydrocarbon chains. The bands around 1100 cm.$^{-1}$ are close to polyethylene bands assigned by Krimm, *et al.*,[23] to C–C vibrations of amorphous polyethylene. They seem polarized roughly perpendicularly to the hydrocarbon chains and might arise in this case from C–C vibrations of chains with definite length.

Vaccenic Acid.—Figure 3A shows the infrared spectra of vaccenic acid observed with the electric vector parallel to *a* and *b*, 3B with the electric

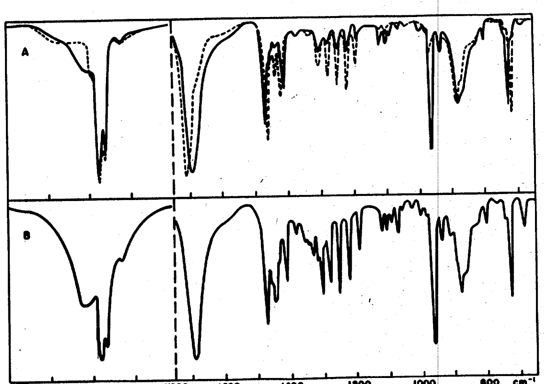

Fig. 3.—Infrared spectrum of vaccenic acid: A, electric vector along *a* (solid line) and *b* (dotted line); B, electric vector along a′.

vector along a′ (compare with Fig. 1). The spectra obtained with the electric vector along a′ and a″ were identical. The same is true for spectra obtained with the electric vector along b′ and b″. The absorption bands are listed and described in Table II. The polarization and position of the bands arising from factor modes of the substructure show a striking similarity to corresponding stearic acid bands. This fact, together with the identity of the a′, a″ and b′, b″ spectra, suggests that in vaccenic acid orthorhombically packed hydrocarbon chains are built into an orthorhombic main structure.

If the dimers have a center of symmetry (as suggested by the known structures of saturated fatty acids,[3] by the infrared work of Hadži and Sheppard[8] and by the main features of the spectrum of vaccenic acid), the structure probably belongs to the holohedral class, with at least four dimers in the unit cell occupying C_i sites of one of the space groups isomorphous with D_{2h}.[24] The packing within one layer of dimers, illustrated in Fig. 4B, is essentially determined by the long spacing,[4] the symmetry of the dimers and by the hydrocarbon substructure. Figure 4A shows the structure of a saturated form C acid[3] for comparison; Fig. 4C

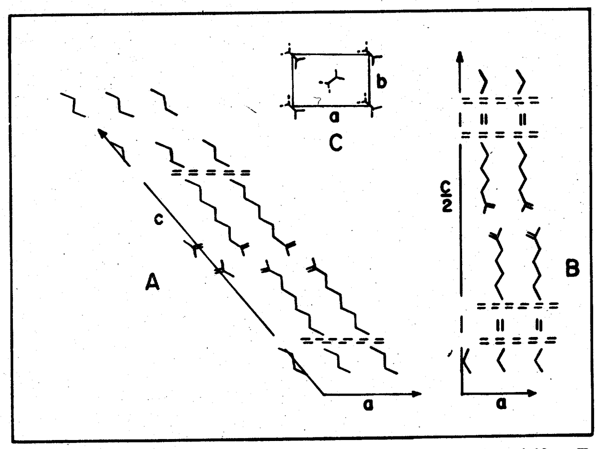

Fig. 4.—A, schematic structure of a form C acid[3]; B, proposed schematic structure of vaccenic acid; C, the orthorhombic subcell projected along the main axes of hydrocarbon chains.

illustrates the orthorhombic hydrocarbon substructure. It is difficult to say anything about the relationship between consecutive layers of dimers, which is related to the packing of the methyl end groups (except that the over-all structure is probably orthorhombic holohedry, as discussed above). A packing corresponding to D^{16}_{2h} would require a mirror plane parallel to *ab*. Similar configurations containing, for instance, a $^1/_2(a + b)$ glide plane are also possible.

A factor group isomorphous with D_{2h}, with four C_i dimers in the unit cell would cause each infrared-active site mode to split into three infrared-active branches, polarized along the three mutually perpendicular crystal axes, and a fourth inactive mode. Because of the arrangement of the molecules in the crystal, some of the active branches are expected to have very low intensities, a situation somewhat similar to crystalline benzene.[30] The relative intensities of the branches can be used to draw some additional qualitative conclusions about the shape and packing of the molecules. The *a* branch of the 965 cm.$^{-1}$ =C—H out-of-plane deformation band is very strong, the *b* branch very weak, indicating that all double bonds are nearly parallel in the projection along the *c*-axis, despite the orthorhombic Bunn type packing of the main portions of the hydrocarbons chains. The *b* polarization of the =C—H stretching band at 3015 cm.$^{-1}$ is in agreement with this observation, although the 3015 cm.$^{-1}$ band (as observed with

(30) S. Zwerdling and R. S. Halford, *J. Chem. Phys.*, **23**, 2221 (1955)

available instrumentation) alone is too weak and ill-resolved to permit positive conclusions. The strong *a* and *b* branches of the C=O stretching band around 1700 cm.$^{-1}$ show that the carboxyl groups are again tilted in this projection. The hydrocarbon chains must be considerably twisted—probably because of relatively strong interactions between the π orbitals of the double bonds—to account for these observations.

The 1190–1352 cm.$^{-1}$ region of the spectrum deserves a few remarks. The carboxyl deformation band usually found in this region cannot be distinguished from the series of five equally spaced relatively strong bands, which are related to the chain length between the carboxyl group and the double bond.[31] The five bands have components along all three axes and therefore probably do not arise in a simple manner from parallel or perpendicular modes of isolated chains. The four much weaker bands between 1352 and 1313 cm.$^{-1}$, on the other hand, are polarized essentially along the *c*-axis, which is compatible with a CH_2 wagging assignment.

(31) H. Susi, *Anal. Chem.*, in press.

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